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Mechanistic Studies of Polymeric Samples Exposed Aboard STS VIII

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ABSTRACT

The early Shuttle flights and the attendant opportunity to deploy material samples to the near-earth space environment, along well defined trajectories and accompanied by detailed characterization of these samples prior to and following the flight exposure, have brought to light several novel phenomena associated with interaction of these materials with the space environment. The Jet Propulsion Laboratory (JPL), in coordination with other National Aeronautics and Space Administration (NASA) centers, has carried out a research program to study the material degradation and oxidation processes caused by interaction of these materials with atomic oxygen at an interaction energy of 5 electron volts (eV). In addition, the interaction of energetic atomic oxygen with materials is believed to be responsible for the "shuttle glow" first observed during the flight of Space Transportation System (STS) III. The shuttle glow phenomenon has been extensively studied and modeled because of its long-range potential impact on optical communication schemes and its more immediate impact on the Space Telescope. This report summarizes the results of certain material degradation and erosion experiments carried out aboard the STS VIII flight, which occurred between August 30, 1983 and September 5, 1983. Based on these data, a generic degradation model has been developed for common structural polymers.

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I. STS FLIGHT VIII HARDWARE AND OXYGEN ATOM FLUENCE

Details of the STS VIII exposure experiment have been reported elsewhere[1]. In STS VIII, two experimental trays were placed on a payload carrier at a forward location in the orbiter bay. These trays held samples of materials in the form of discs as well as strips. Figure 1 illustrates the placement of these two trays with respect to the orbiter. All strip samples were mounted on calibrated heating plates to evaluate the effect of temperature on degradation. Templabels were used to monitor sample temperatures in flight. Temperatures of 75°F, 150°F, and 250°F were planned. Readings from templabels, however, indicated that temperatures of 75°F, 250°F, and 260°F were reached during flight. The total flight duration was 140 hours with four principal attitudes acquired during the mission. Table I summarizes the flight attitudes. The principal material exposure attitude was ±XLV, payload bay into the velocity vector, and is illustrated in Figure 1. This attitude was acquired three times during the mission and the total oxygen atom fluence was calculated to be $\approx 2.7 \times 10^{-20}$ atoms/cm^2 over a 41-hour duration. This number was derived from Goddard Space Flight Center (GSFC) atmospheric density models and NOAA solar activity predictions for the actual flight trajectories.

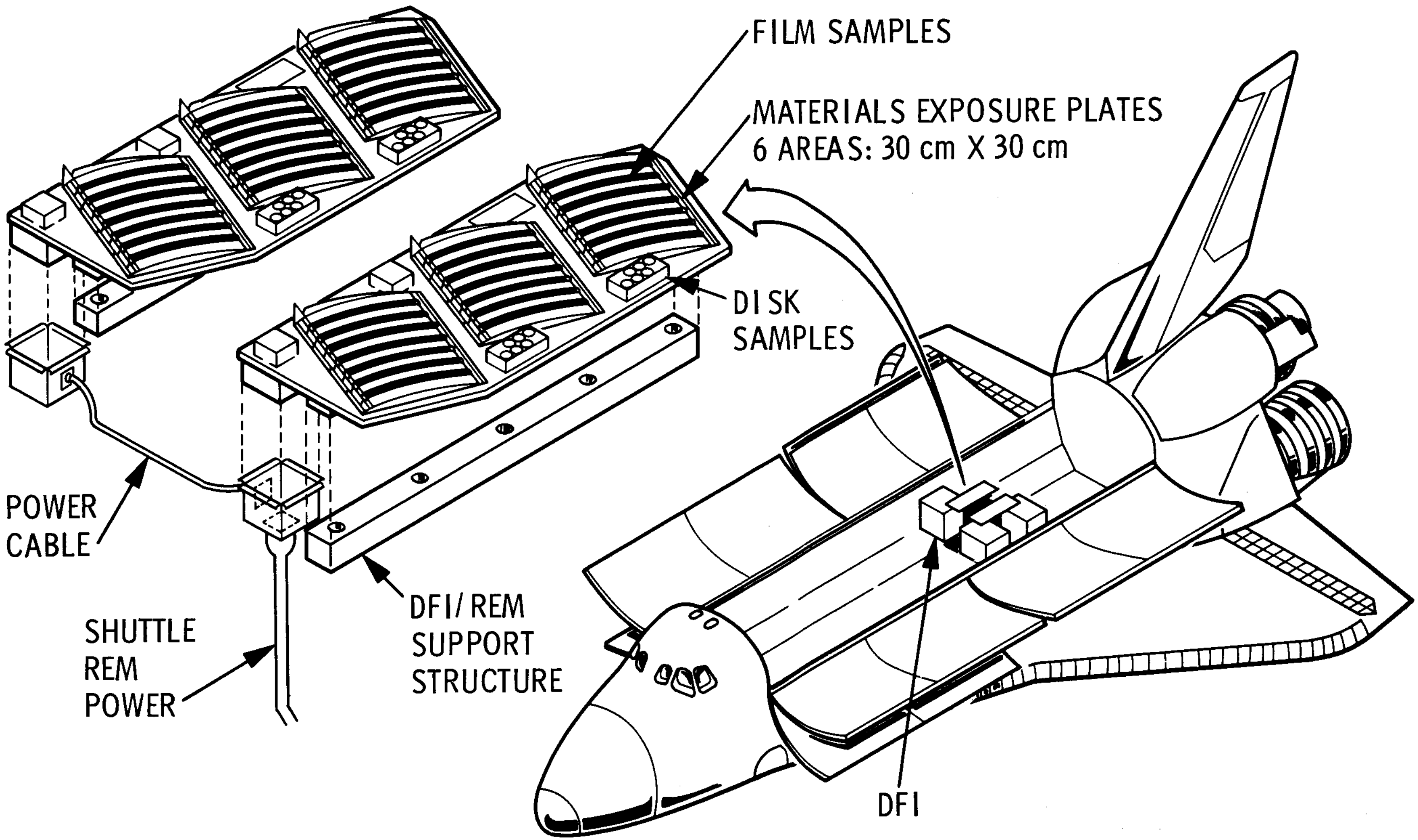

Figure 1. Material Tray Configuration.

Table I. STS Flight VIII Attitude Summary

ATTITUDE	ORBITS	HOURS
-ZLV NOSE FWD	35	52.83
-XSI ORB RATE	10	15.67
-ZLV FREE DRIFT	9	12.92
±XLV PLB FWD	27	41.17
+XLV PLB NORTH	1	1.33
STAR TRACKER TESTS	2	2.75
KuBd/IMU ALIGNMENT	8	12.00
TAIL GLOW	1	1.50
TOTALS	93	140.17

II. EXPERIMENTAL

A. Sample Preparation

Six types of disc samples (1" in diameter) and two types of strip (3"x1") samples were prepared for the STS flight VIII exposure experiment. Polymethylmethacrylate (PMMA) beads were purchased from Polysciences, Inc. at two intrinsic viscosities: 1.4 and 0.4. The samples were compression molded at 177°C between teflon-coated Kapton sheets. A film of 0.007 in. thickness was obtained for the 0.4 viscosity material and a thicker film of 0.044 in. was prepared from the 1.4 intrinsic viscosity PMMA. Polyethylene (PE) with a density of 0.915 and polystyrene (PS) were molded at 150°C and 177°C, respectively, as received from Polysciences, Inc. Film thicknesses of 0.005 in. were made. Polysulfone (Union Carbide Udel 1700) pellets were dried in a vacuum oven at 150°C for 3 days and then compression molded at 293°C to form 0.005 in. thick films. No mold releasing agent which contains silicon was used in any compression molding in order to avoid sample surface contamination. Instead, samples were molded between two sheets of teflon-coated Kapton films. Teflon was used for ease of sample release. Kapton (DuPont 500H) and teflon-coated Kapton (DuPont F131) were cut from as-received sheets. The above films were cut into approximately 1-inch diameter discs.

Carbon-filled polyurethane-based Z-306 chemglaze paint samples were also flown on STS VIII. This chemglaze paint is of interest to study because of its display of the material glow phenomenon believed to be a consequence of interaction of the surface layer with energetic oxygen atoms in the low-earth orbit environment. Samples were provided by Marshall Flight Center, Huntsville, Alabama.

Two types of strip samples were prepared for exposure and subsequent mechanical testing: 3" X 1" PMMA (viscosity 0.4) and polysulfone films. Table II lists various tests that were performed on the samples. Table III shows the weight loss data.

Table II. Tests Performed on Samples Flown on STS VIII

MATERIAL	ESCA	HPLC	TENSILE STRESS-STRAIN	RR	WEIGHT LOSS	RHEOVIBRON
PMMA (Viscosity 1.4)	X	X	X		X	
PMMA (Viscosity 0.4)	X	X	X		X	
POLYETHYLENE	X			X	X	
POLYSULFONE (Udel 1700)	X	X	X	-	X	
POLYSTYRENE	X				X	
KAPTON (DuPont 500H)	X			X	X	X
KAPTON (DuPont F131)	X			X	X	X
Z-306 CHEMGLAZE PAINT	X					

X = Completed

\- = Attempted but unable to obtain data

Table III. Weight Loss Data

MATERIAL	WEIGHT LOSS mg/cm^2
POLYETHYLENE	1.3 ± .2
POLYMETHYLMETHACRYLATE:	
(VISCOSITY - 1.4)	1.2
(VISCOSITY - 0.4)	2.1
POLYSULFONE	1.1
KAPTON (DuPont 500H)	1.3
KAPTON (DuPont F131)	<0.2
POLYSTYRENE	0.8

B. Analysis

The following analyses were carried out on the STS VIII samples:

1) ESCA - Electron Spectroscopy for Chemical Analysis was performed on a Hewlett Packard ESCA photoelectron spectrometer Model 5958. This test provides data on the elemental composition of the surface (approximately the top 50 - 100 Å) of each sample. High-resolution spectra were curve-fitted

to resolve the presence of multiple atomic components and estimates of concentration in atomic percentage.

2) HPLC - High Pressure Liquid Chromatography was carried out by a Water Associates Model 6000A chromatogram. Four-column (10^5 Å, 10^4 Å, 10^3 Å, and 500 Å) microstyrogel separation was performed. Polystyrene was used for molecular weight calibration and chloroform was used as the solvent.

3) Tensile Stress-Strain Tests - Tensile stress-strain tests were carried out by stretching the sample in a tensile mode at a pre-set crosshead speed in a table Model-TM-Instron machine.

   This Instron was equipped with an environmental chamber with temperature control to ±0.5°C. The load was measured as a function of time in a strip chart recorder. Tests were performed at a strain rate of 0.02 min^{-1}. Test temperature was 25°C.

4) RR - A CW Ar^+ and Kr^+ ion laser and a CW Ar^+ ion pumped dye laser were used as the tunable excitation source for resonance Raman spectroscopy. In order to select the best excitation and minimize the fluorescence background, several excitation wavelengths were used.

5) Weight Loss - Samples were measured using a Mettler Type #15 160g balance with a sensitivity of 0.1 mg.

6) Rheovibron - Dynamic mechanical testing was performed using a Rheovibron Dynamic Viscoelastometer Model DDV-II. Test temperature range was -133 to 240°C, at 11-Hz frequency.

III. RESULTS

A. Polyethylene (PE)

Polyethylene has the simplest possible chemical structure of all polymers and, hence, the fewest possible modes of interaction with energetic oxygen atoms. It was therefore used as a model system. Since PE is known to undergo slow terrestrial oxidation, extreme care was taken when samples of PE were prepared to minimize this oxidation process. The weight loss of disc samples flown aboard STS VIII was found to be 1.3 ± 0.2 mg/cm^2. Erosive weight loss amounted to 7% of the total sample weight. Control and exposed surfaces of PE have similar Raman spectra, as shown in Figure 2. There is a hint of the formation of a C-O bond on the exposed surface as evidenced by the broad peak at 1090 cm^{-1}. Hence, the thickness of the residual oxidized layer was expected to be very small. Both low- and high-resolution ESCA were performed in order to characterize this layer. Figure 3 is the ESCA spectra of control and exposed surfaces of polyethylene.

High-resolution ESCA spectra of the carbon in PE were illustrated in Figure 4. The integrated area under each peak was used to calculate the percent composition and the results are listed in Table IV. It is clear that the chemical composition of the exposed surface layer (50Å) includes 9.9 atom percent oxygen, in contrast to 0.8 atom percent on a control surface (backside of the same sample). High-resolution ESCA on the carbon peak also indicated that oxidized carbon atoms were formed on the exposed surface. It is of interest to note that both singly oxidized (C_2), as well as doubly oxidized (C_3) carbon atoms, including carboxylic acid groups were detected on the exposed surface. The ESCA data on the composition of this residual oxidized layer lead to the conclusion that the initial or the primary interaction of the PE surface with atomic oxygen creates a partially oxidized intermediate state which may undergo volatilization or subsequent further oxidation leading to the formulation of carboxyl groups found by ESCA spectroscopy.

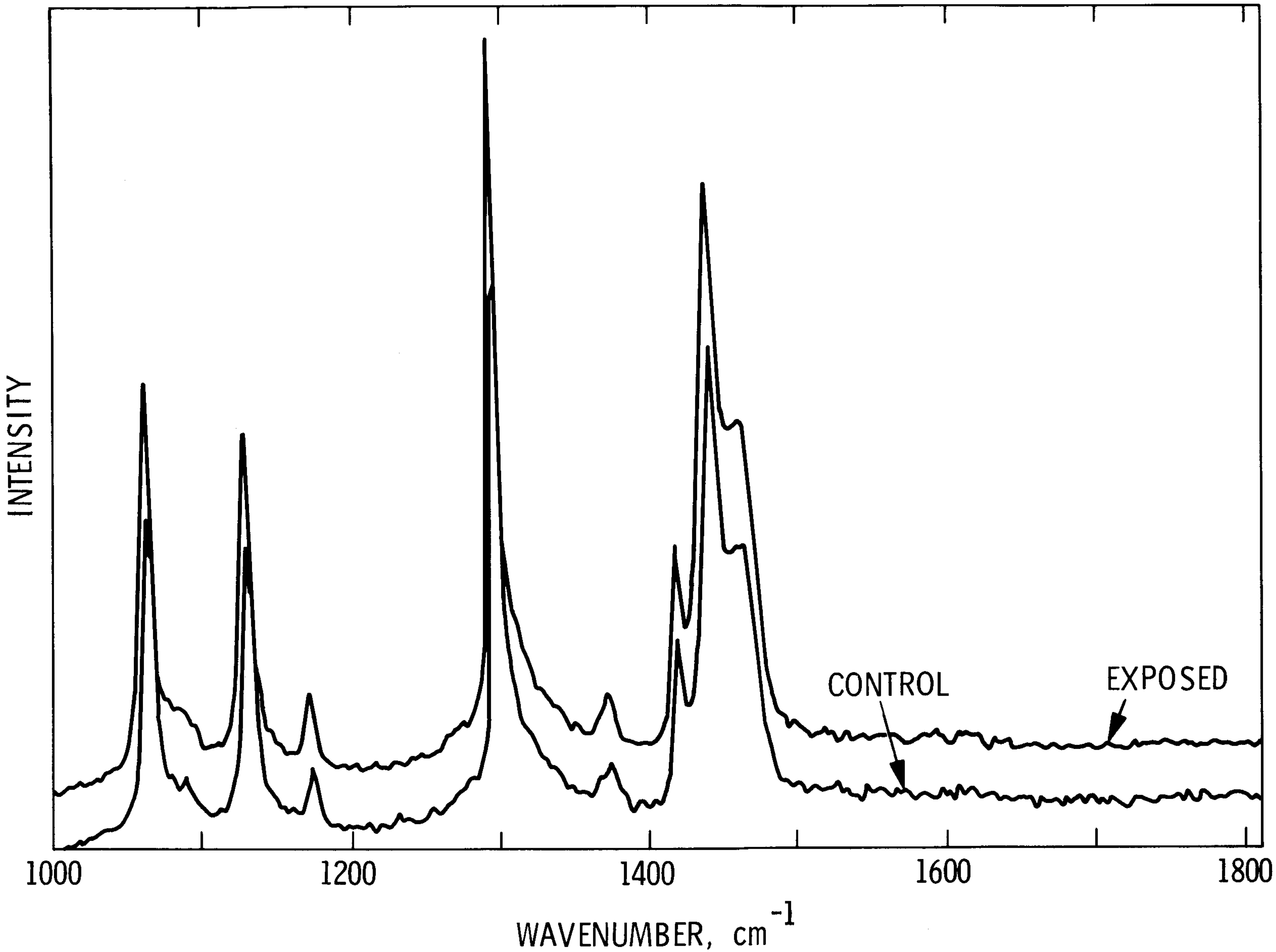

Figure 2. Raman Spectra of Polyethylene.

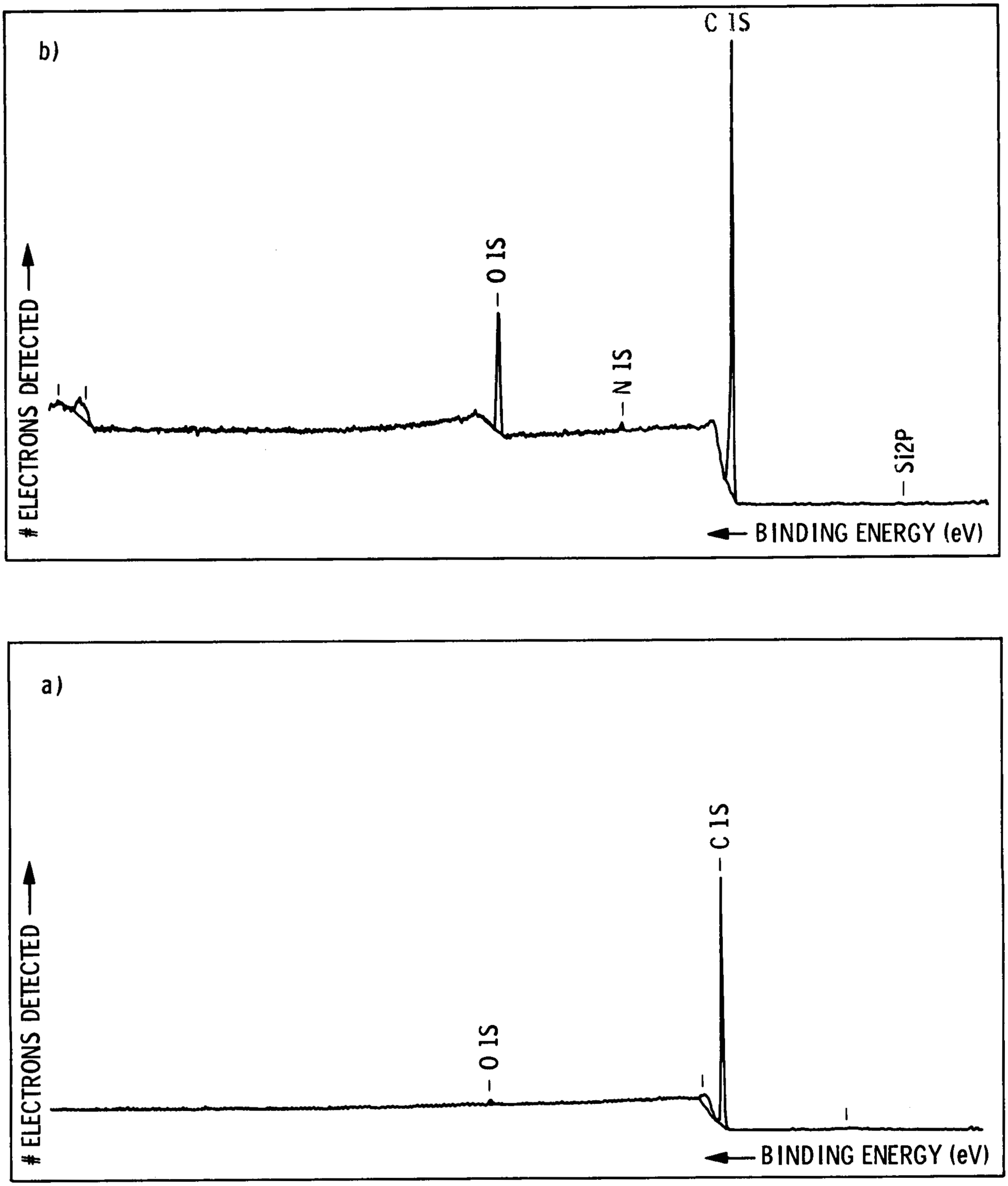

Figure 3. ESCA Spectra of a) Control and b) Exposed Surfaces of Polyethylene.

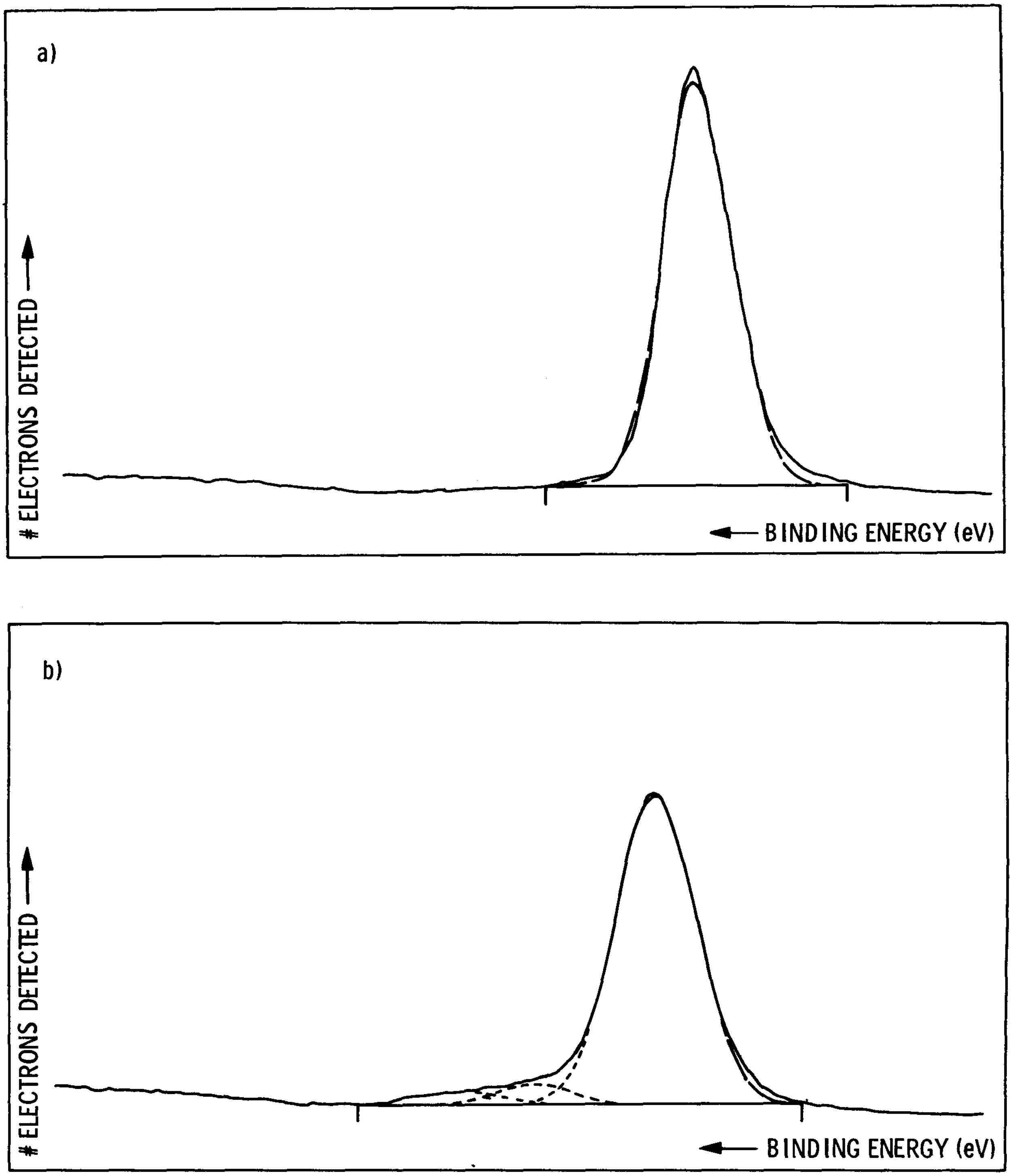

Figure 4. High-Resolution ESCA Spectra of the Carbon in a) Control and b) Exposed Surfaces of Polyethylene.

Table IV. Percent Composition of Polyethylene Surfaces from ESCA

	% COMPOSITION				
	C_1	C_2	C_3	O	O/C
THEORETICAL	100	--	--	--	--
CONTROL	99.2	--	--	0.8	0.01
EXPOSED	81.5	4.5	3.1	9.9	0.11

C_1: C-C C_2: C=O, O-C-O C_3: O-C=O

The density of PE before and after exposure was measured and is shown in Table V. Within experimental error, density data showed no detectable differences. This result indicates that crystalline segments erode at the same rate as the amorphous segments, since otherwise an increase in the crystallinity could be expected in the residual film.

Table V. Density Measurement of Polyethylene

CONDITION	DENSITY gm/cm^3
CONTROL	0.916
EXPOSED	0.917

B. Polymethylmethacrylate (PMMA)

PMMA of two intrinsic viscosities (0.4 and 1.4) were used. While the high-viscosity (1.4) sample showed a weight loss of 1.2 mg/cm^2, the low-viscosity one (0.4) showed almost twice as much weight loss, i.e. 2.1 mg/cm^2. Results of HPLC analysis are shown in Table VI and Figure 5. These data indicated the low-viscosity PMMA contained a substantial amount of a low molecular-weight component which would be susceptible to volatilization. This may account for the unusually high weight loss observed for this sample.

ESCA analysis was also carried out on both disc samples. Within experimental error (±2%), both high- and low-viscosity samples exhibit similar results and are summarized in Table VII.

It is interesting to point out that while PMMA was suffering weight loss due to erosion, the chemical composition of the eroded surface remained unchanged.

Tensile stress-strain tests were also performed on PMMA strips. Stress-strain data were obtained after accounting for changes in the thickness of the specimen due to erosion. Results showed no detectable change in the tensile modulus and are illustrated in Figure 6.

The HPLC data indicate that chain scission and unzipping processes were occurring in PMMA on oxygen atom interaction. Since the oxidized material would be volatilized under these conditions, the eroded surface would retain the chemical composition of this original material. The extent of the molecular weight loss is insufficient to cause a measurable decrease in deformation properties; hence, no change in the tensile modulus is observed.

Table VI. Summary of Results of HPLC on PMMA

	TESTING CONDITION	$\bar{M}_n$	$\bar{M}_w$
1.4 VISCOSITY	CONTROL	192,000	404,000
	EXPOSED	166,000	357,000
0.4 VISCOSITY	CONTROL	143,000	250,000
	EXPOSED	101,000	209,000

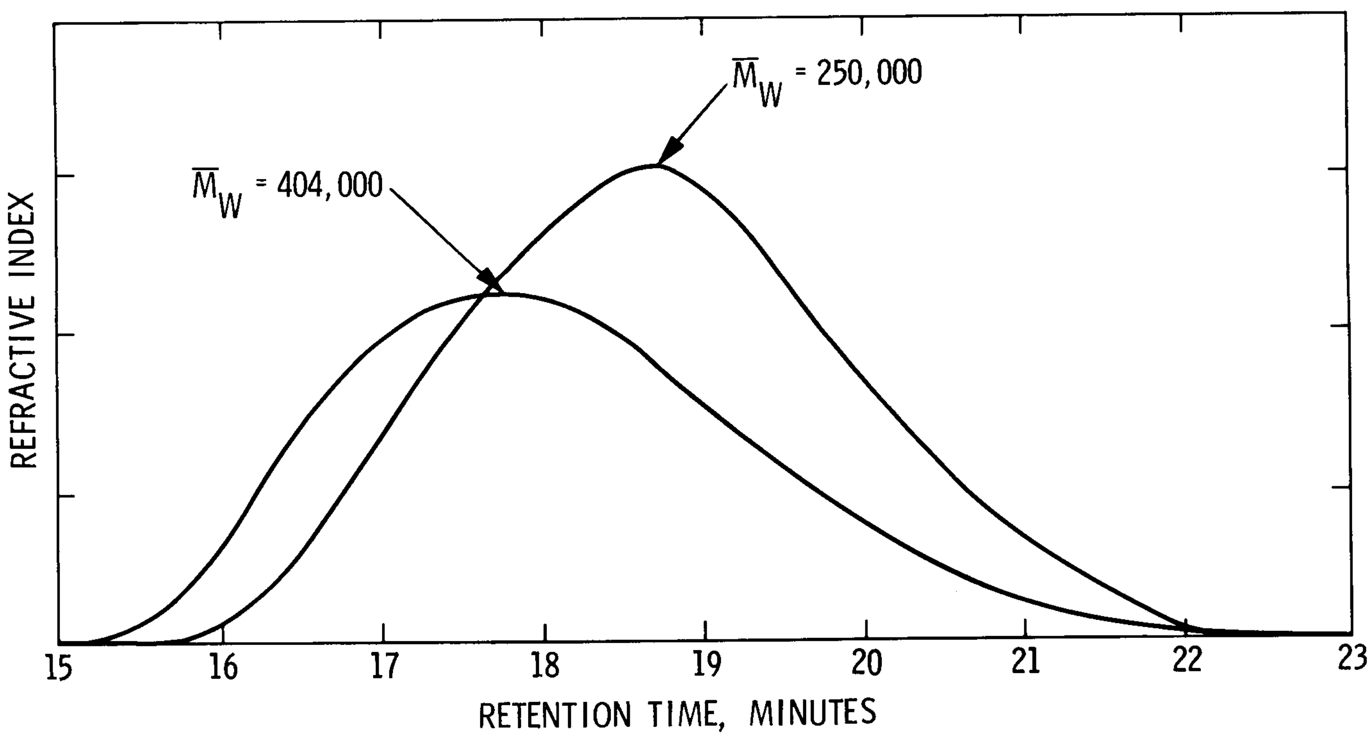

Figure 5. HPLC of Polymethylmethacrylate.

Table VII. Percent Composition of Polymethylmethacrylate Surfaces from ESCA

	% COMPOSITION				O/C
	O	C_1	C_2	C_3	
THEORETICAL	29	43	14	14	0.41
CONTROL	24	48	14	13	0.32
EXPOSED	26	45	14	14	0.36

C_1: C-C C_2: C-O C_3: O-C=O

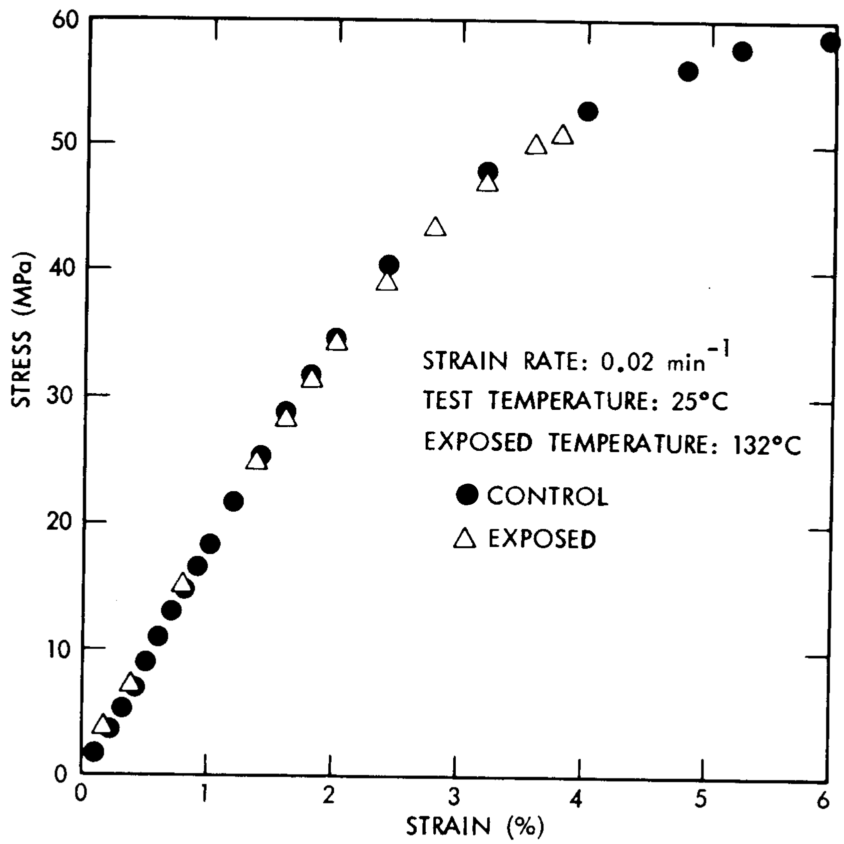

Figure 6. Stress-Strain Curves of PMMA Returned from STS Flight VIII.

C. Polysulfone

The weight loss of a disc sample of polysulfone was found to be 1.1 mg/cm^2, which amounts to 3.5% change of the total sample weight. An attempt to obtain a resonance Raman spectrum of polysulfone failed due to the intense fluorescence and photo-instability of the sample at visible wavelengths (600-450 nm). Results of ESCA analysis are shown in Table VIII. The control surface matches well with that of a pure polysulfone. The exposed surface, however, showed a 10% decrease in hydrocarbon concentration and a 7% increase in oxygen content.

Tensile stress-strain measurements were carried out on the strip polysulfone samples and the results are shown in Figure 7. A substantial drop in the tensile modulus was observed as a result of atomic oxygen exposure. The onset of yield is found in the exposed samples at around 3% strain.

The HPLC data indicate substantial loss of molecular weight due to chain scission. This decrease in molecular weight causes a decrease in mechanical properties such as the tensile modulus, reflected in the tensile stress-strain data. Presumably the chain scission is initiated through oxidation of the polysulfone chain, probably at the phenyl nucleus. HPLC results are summarized in Table IX.

Table VIII. Percent Composition of Polysulfone Surfaces by ESCA

	% COMPOSITION							
	C_1	C_2	C_3	S	O_1	O_2	N	O/C
THEORETICAL	72	13	-	3.1	6.3	6.3	-	0.15
CONTROL	72	7.4	2.2	2.6	8.3	5.8	1.5	0.16
EXPOSED	62	8.8	2.6	3.4	10.5	10.5	-	0.29

C_1: C-C C_2: C-O C_3: shake-up S: SO_2 O_1: S=O, C=O O_2: C-O

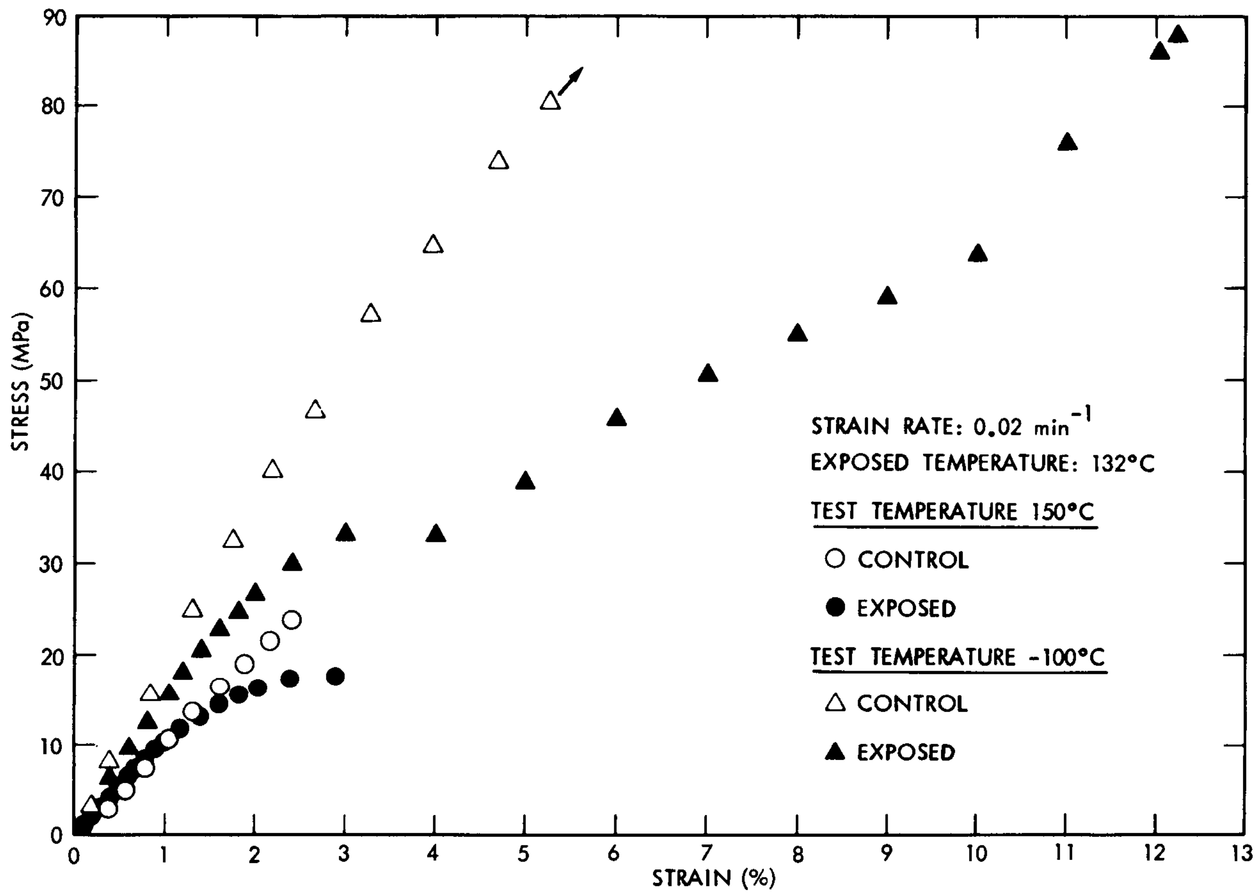

Figure 7. Stress-Strain Curves of Polysulfone Returned from STS Flight VIII.

Table IX. Summary of HPLC Results on Polysulfone

	TESTING CONDITION	$\bar{M}_n$	$\bar{M}_w$
DISC	CONTROL	57,400	86,700
	EXPOSED	25,700	73,400
STRIP	CONTROL	51,700	94,700
	EXPOSED	35,600	74,600

D. Kapton and Teflon-Coated Kapton

An average weight loss of 1.3 mg/cm^2 was observed on the exposed DuPont (500H) disc. No detectable weight loss could be determined on the teflon-coated Kapton DuPont (F131) samples. Resonance Raman spectra of Kapton before and after exposure are illustrated in Figure 8. The only notable difference is the disappearance of the 1600 cm^{-1} phenylene peak. This result was reported earlier for the exposed Kapton sample returned from STS II, III, and V missions. Results of ESCA analysis on Kapton are shown in Table X. Rheovibron measurements were taken in triplicate at room temperature and are summarized in Table XI.

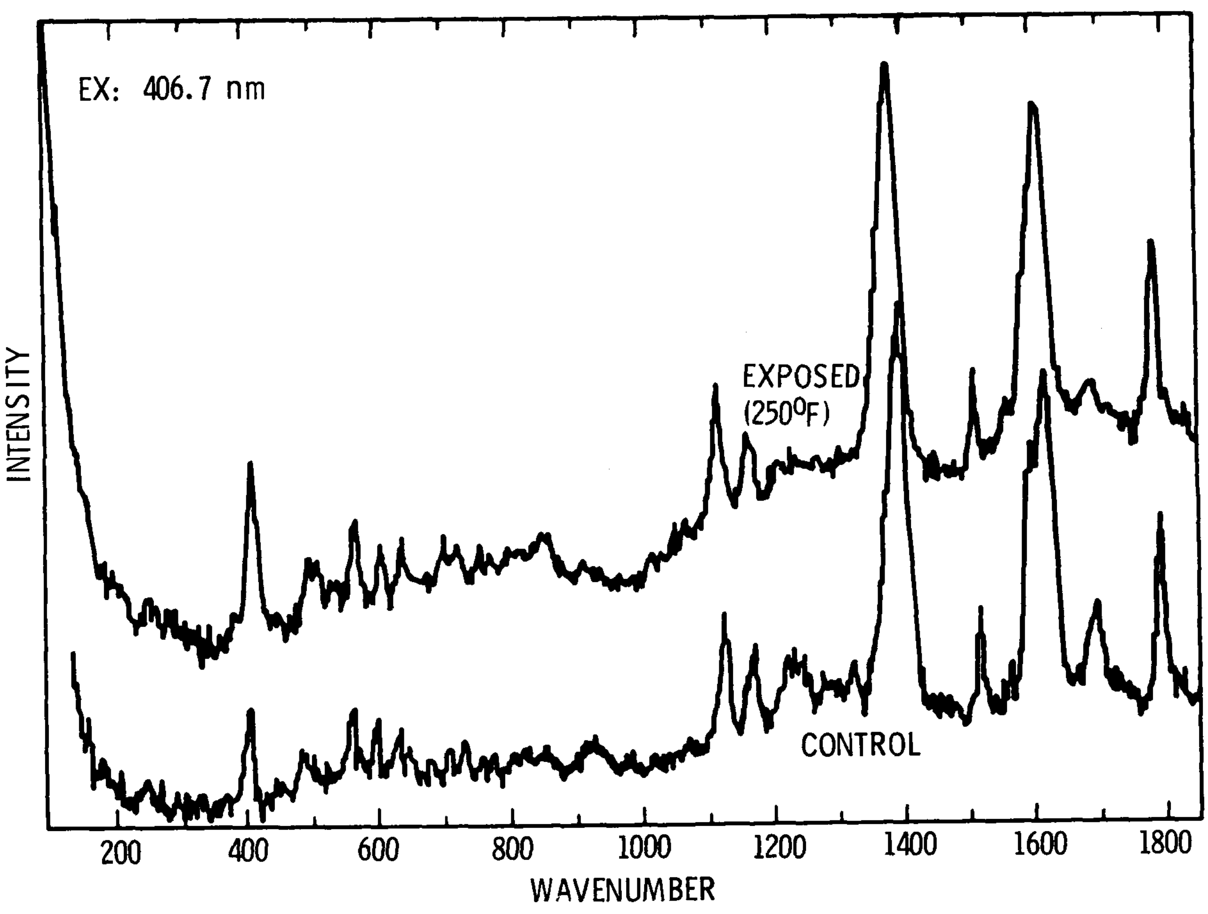

Figure 8. Resonance Raman Spectra of Kapton Before and After Exposure.

Table X. Percent Composition of Kapton Surfaces from High-Resolution ESCA

	% COMPOSITION						
	C_1	C_2	C_3	O_1	O_2	N	O/C
CONTROL	48	14	14	14	3.4	6.9	0.23
EXPOSED	29	30	14	15	4.1	7.1	0.26

C_1: C-C C_2: C-O,C-N C_3: N-C=O O_1: C=O O_2: C-O

Table XI. Dynamic Modulus Data for Kapton Flown on STS VIII

MATERIAL	TESTING CONDITION	E, 10^5 psi
KAPTON	CONTROL EXPOSED	26.4 ± 0.2 26.1 ± 0.6
TEFLON-COATED KAPTON	CONTROL EXPOSED	26.8 ± 0.2 23.5 ± 0.3

E. Polystyrene

Polystyrene has the simplest chemical structure for an aromatic polymer and is therefore used as a model compound. The average weight loss of a disc sample is 0.8 mg/cm^2, which is substantially lower than the other samples exposed. Surface composition from high-resolution ESCA analysis is listed in Table XII.

Table XII. ESCA Summary of Results on Polystyrene

	% COMPOSITION									O/C
	C_1	C_2	C_3	C_4	P_1	P_2	Ca	Zn	O	
THEORETICAL	100	-	-	-	-	-	-	-	-	-
CONTROL	97	-	-	-	-	-	-	-	2.2	0.02
EXPOSED	28	14	3.7	2.0	1.4	4.1	11	1.7	34	0.71

C_1: C-C C_2: C-O C_3: O-C=O C_4: shake-up P_1: PO_4^{3-} P_2: P_2O_5

The exposed surface was contaminated as evidenced by the detection of phosphate salts, calcium, and zinc (P_1, P_2, Ca, and Zn). The additional weight of these contaminants may be partially responsible for the low erosion rate of the polystyrene observed. Note that the hydrocarbon (C_1) content was reduced from 97% to 28%, while the oxygen content rose from 2.2% to 34% as a result of exposure. This rise in oxygen content on the exposure surface is substantial, in spite of the contribution from PO_4^{3-} and P_2O_5.

F. Z-306 Chemglaze Paint

Surface composition of the chemglaze paint was also testd by ESCA Figures 9 and 10 are the high-resolution carbon and oxygen ESCA spectra of Z-306, respectively. The percent composition of the surface is summarized in Table XIII.

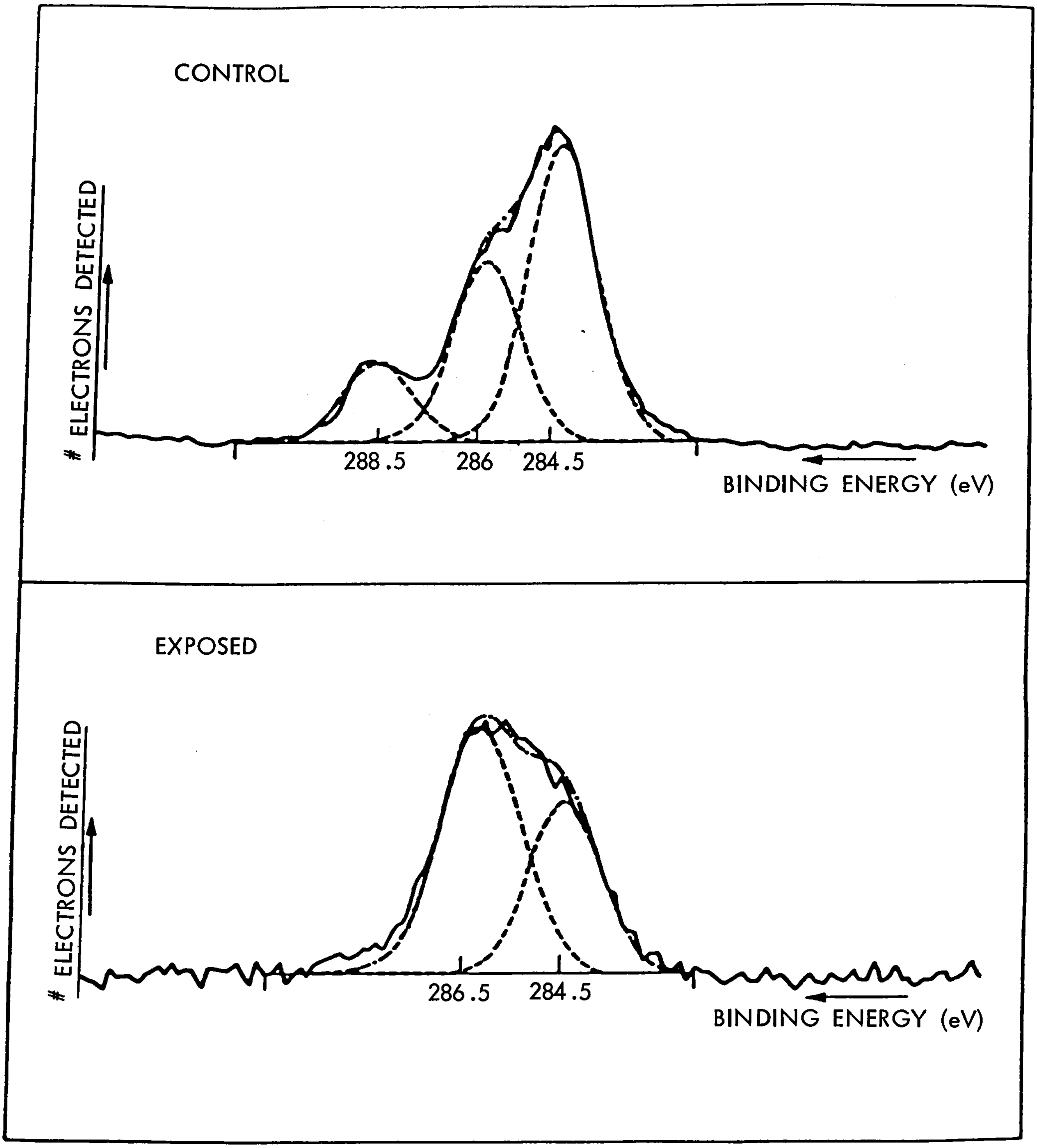

Figure 9. High-Resolution ESCA Spectra of Carbon on Z-306 Surfaces.

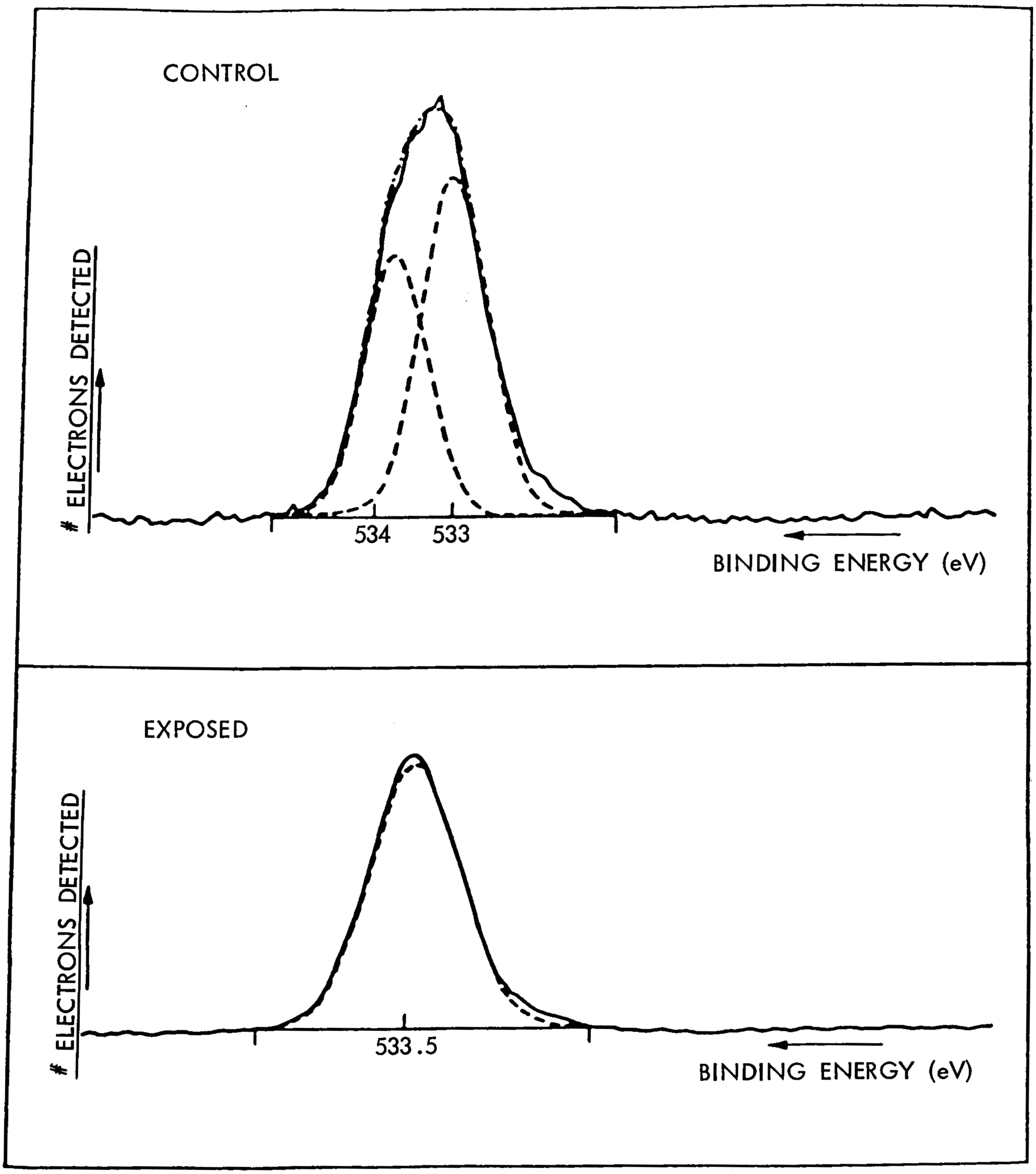

Figure 10. High-Resolution ESCA Spectra of Oxygen on Z-306 Surfaces.

Table XIII. Surface Composition of the Z-306 Paint Aboard STS VIII

	% COMPOSITION						
	C_1	C_2	C_3	O	Si	F	N
CONTROL	39	23	10	26	-	-	1.7
EXPOSED	6.5	11	-	57	24	1.6	-

C_1: C-C C_2: C-O C_3: O-C=O Si = SiO_2

IV. DISCUSSION

The following generic model of interaction of organic materials with energetic oxygen atoms has been developed based on the results of the physicochemical characterization of samples flown on STS VIII (see Figure 11):

$$P + O \xrightarrow{k_1} PO$$

$$PO + O \xrightarrow{k_2} PO_2$$

$$PO + O \xrightarrow{k_3} V_1 + P$$

$$PO_2 + O \xrightarrow{k_4} V_2 + P$$

When the polymer surface (P) is exposed to an energetic oxygen atom (O), a polymeric intermediate such as an oxide (PO or PO_2) is formed. The intermediate may then encounter another oxygen to form either PO_2 or a volatile product (V_1) plus the original polymer (P). PO_2 may also react further with oxygen to form a different volatile product (V_2), thus, regenerating the polymer. When volatilization of the product occurs, it results in mass loss and contributes to the weight loss experienced by most of the samples flown (see Table III). Therefore, the extent of degradation of samples is controlled by the amount of oxide formed. The mode of degradation, however, depends on the rate of depletion of oxides (PO and PO_2). If the rate of depletion is relatively fast, the oxygen concentration accumulating on the polymer surface will be low and the sample will undergo weight loss, but with no apparent changes in bulk properties. This appears to be the case for Kapton (DuPont 500H).

The longer the oxides remain on the surface, the higher the oxygen concentration and the lower the weight loss. Bulk properties may change, however, if the oxides remain long enough to react chemically with the

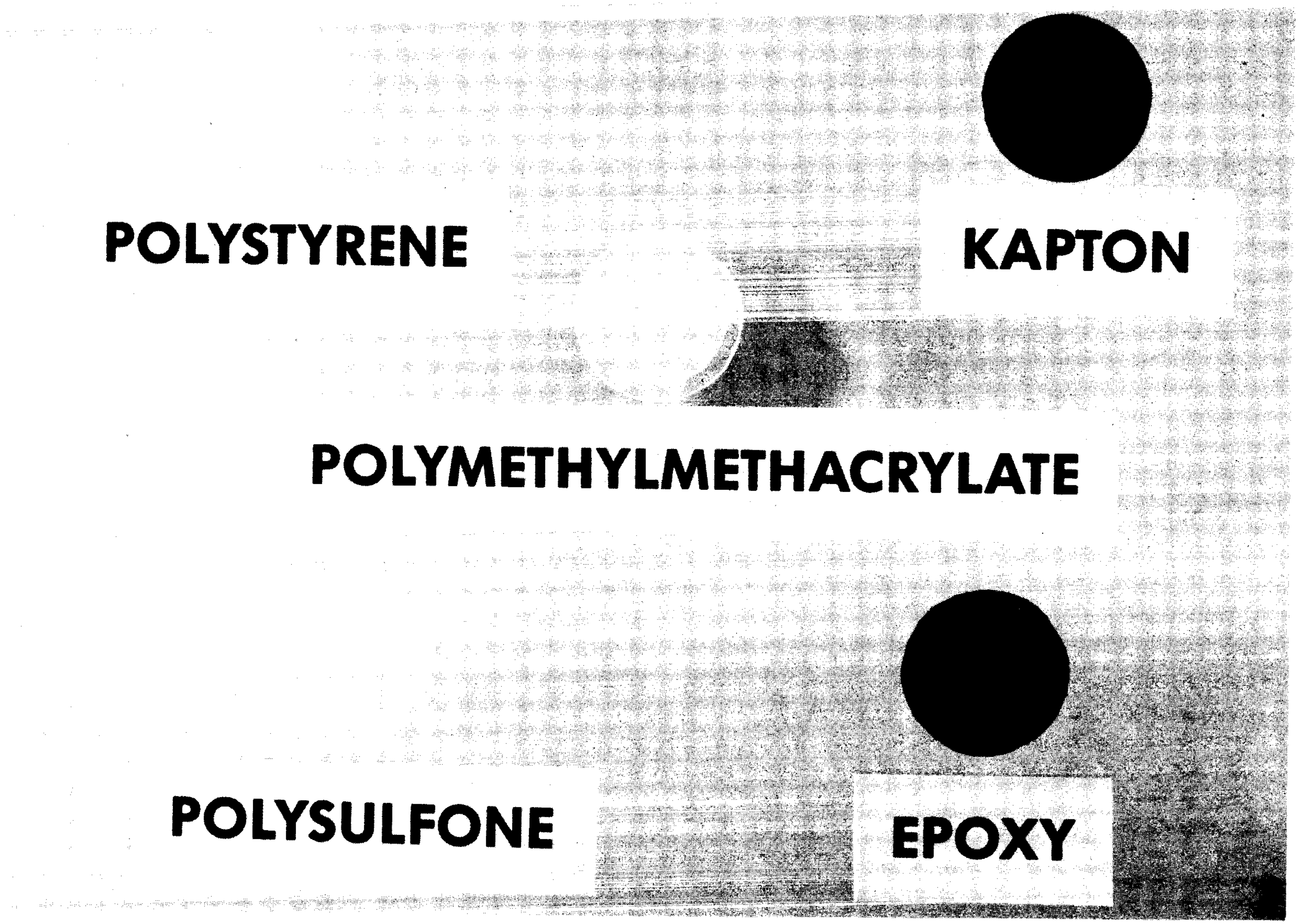

Figure 11. Polymer Samples Eroded by Atomic Oxygen During STS VIII.

polymer. ESCA data indicate there are chemical changes occurring on the surface (50 Å) of the polyethylene film. A 10% oxygen composition was found on the sample surface versus 0.8% on the unexposed side. Density measurements, however, failed to indicate any change in the bulk between the control and exposed films.

Oxide concentrations were also calculated from ESCA data for polysulfone and used as indicators of the oxygen buildup on the sample surface. The surface of the polysulfone sample displayed a 7% increase in oxygen content. There is also a significant change in bulk properties indicated by tensile stress-strain data. Teflon-coated Kapton (DuPont F131), on the other hand, experienced no detectable loss of weight, which may correspond to a slow buildup of oxides on the surface. Rheovibron measurements showed a decrease in the dynamic modulus of 3.3×10^5 psi between control and exposed samples.

When analyzing oxide concentration measurements obtained from ESCA data, all exposed samples (with the exception of PMMA) showed an oxygen concentration buildup. PMMA also experienced a large weight loss, but with little chemical changes. Tensile stress-strain data indicate no appreciable difference between the control and exposed samples.

One theory to explain these data is that PMMA is known to unzip under certain circumstances once degradation is initiated. This would give rise to weight loss, but with no apparent chemical change on the surface since fresh PMMA chains are always brought to the surface as these oxidized chains undergo depolymerization and subsequent removal through evaporation. The mechanism at play here seems to be the unzipping of the polymer chain.

The chemical composition of the Z-306 chemglaze control surface is what one would expect of the paint. This paint is a carbon-filled polyurethane embedded with silica. Further analysis of the oxygen sites in the control surface indicates that both carbonyls and C-O (esters, ethers) are present. The eroded surface, in contrast, is 70 to 80% SiOx. It also contains minor amounts of carbonyl groups and some fluoride. These data indicate that the erosion proceeds until a continuous layer of SiOx is left on the surface, thus, providing protection from further attack by the energetic oxygen atoms.

V. CONCLUSION

A set of polymeric films were exposed to the low-earth orbital environment aboard STS VIII. Pre- and post-flight characterization studies were performed on each sample. These studies indicated that:

1) A residual oxidized layer was found on most, but not all, samples. The composition of this layer and its thickness reflected the overall mechanism of interaction of these materials with atomic oxygen, leading to erosion.

2) Certain samples, such as polysulfone, showed changes in bulk properties, while other samples, such as PMMA, showed no change in bulk properties, despite suffering considerable erosion.

3) There was evidence of secondary oxidation in some samples, caused by interaction of atomic oxygen with the oxidized layer.

More detailed studies, especially including in-situ monitoring of volatile degradation products, are needed to further elucidate the mechanism of the erosion process.

VI. REFERENCE

1. Leger, L. J., Visentine, J. T., and Kuminecz, J. F., "Low Earth Orbit Atomic Oxygen Effects on Surfaces," AIAA Paper 84-0548, January, 1984.